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Enhanced transient reactivity of an O-sputtered Au(111) surface

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Abstract

The interaction of SO₂ with oxygen-sputtered Au(111) surfaces ($\theta_{\text{oxygen}} \leq 0.35$ ML) was studied by monitoring the oxygen and sulfur coverages as a function of SO₂ exposure. Two reaction regimes were observed: oxygen depletion followed by sulfur deposition. An enhanced, *transient* sulfur deposition rate is observed at the oxygen depletion point. This effect is specifically pronounced if the Au surface is continuously exposed to SO₂. The enhanced reactivity towards S deposition seems to be linked to the presence of highly reactive, under-coordinated Au atoms. Adsorbed oxygen appears to stabilize, but also to block these sites. In absence of the stabilization effect of adsorbed oxygen, i.e. at the oxygen depletion point, the enhanced reactivity decays on a timescale of a few minutes. These observations shed a new light on the catalytic reactivity of highly dispersed gold nanoparticles.

Introduction

The high reactivity of dispersed gold nanoparticles supported on metal oxide surfaces has recently attracted considerable interest. For example, gold nanoparticles on $\text{TiO}_2(110)$ are very efficient catalysts for the low-temperature oxidation of CO [1], as well as for the decomposition of SO_2 [2]. Various models have been proposed to explain the unusual catalytic properties of gold nanoclusters ranging from metal-support interactions to finite size effects [1]. A new aspect of gold nanoclusters was recently introduced by Rodriguez et al. [2], who performed a theoretical study on the reactivity of under-coordinated Au atoms. The study reveals that under-coordinated Au atoms in Au nanoparticles can play an important role. Specifically, it was demonstrated that SO_2 interacts more strongly with under-coordinated Au atoms than with regular terrace atoms of a $\text{Au}(111)$ surface.

In contrast to the high reactivity of supported Au nanoparticles, bulk metallic gold typically exhibits a low reactivity. For example, Liu et al. observed that SO_2 adsorbs molecularly on $\text{Au}(111)$ at 100 K [3], and desorbs without detectable decomposition at 150 K. Recently, we investigated the interaction of SO_2 with $\text{Au}(111)$ at 300 K, and observed the formation of a two-dimensional gold sulfide overlayer by using large exposures of SO_2 [4]. A possible mechanism for the observed S deposition is the disproportionation of SO_2 into adsorbed S and SO_3 , in which the latter species desorbs. There is precedent for SO_3 formation during SO_2 exposure to oxygen-covered $\text{Cu}(110)$ and oxygen-covered $\text{Ag}(110)$ [5,6]. However, on these surfaces SO_3 does not desorb but

decomposes with increasing temperature, consistent with a recent theoretical investigation [7] based on the bond order conservation-Morse potential method.

In the present work we employed Auger Electron Spectroscopy (AES) to study the interaction of SO₂ with oxygen-sputtered Au(111) surfaces by monitoring the oxygen and sulfur coverages as a function of SO₂ exposure. We explain the observed reaction kinetics of sulfur deposition in terms of an enhanced *transient* reactivity of under-coordinated gold species. The experiments described in this paper contribute to a better understanding of the enhanced catalytic reactivity of supported Au nanoparticles used as oxidation catalysts.

Experimental

The experiments were performed in a UHV system with a base pressure of 5×10^{-11} mbar. The system is equipped with commercial instrumentation for STM, AES and LEED, and details of the experimental setup are published elsewhere [8]. The purity of both, O₂ (Matheson, research purity grade) and SO₂ (Matheson, anhydrous grade) was periodically checked with a residual gas analyzer. SO₂ was dosed by backfilling the chamber at pressures between 5×10^{-7} and 2×10^{-6} mbar (uncorrected ion gauge reading). The Au(111) sample was cleaned by cycles of Ar⁺ sputtering at room temperature (60 min/1000 eV/4 μ A) and annealing (10 min at 900 K followed by one hour at 600 K) until no impurities were detected by means of AES.

Oxygen ion sputtering (500 V, 1 μ A, 300 K) of Au(111) surfaces leads to surface roughening and chemisorption of oxygen as shown below. According to Saliba et al. [9] an O₅₁₉/Au₂₃₉ AES peak-to-peak height ratio of 1.0 corresponds to a oxygen coverage of

~ 0.85 ML. Using this calibration, we observed a oxygen saturation coverage of $0.35 \text{ ML} \pm 0.05 \text{ ML}$ ($1 \text{ ML} = 1.4 \times 10^{15} \text{ cm}^{-2}$). The S coverage was calibrated against the S_{150} AES signal obtained from a $\text{Au}(111)/(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ S surface [4].

In order to study the effect of annealing (and thus decreasing surface roughness) on the reactivity towards SO_2 , some oxygen-sputtered $\text{Au}(111)$ surfaces were annealed to 400 K prior to SO_2 exposure. AES reveals that the oxygen coverage decreases by $\sim 40 \%$ during annealing of oxygen-sputtered $\text{Au}(111)$ surfaces. This can be explained by isothermal desorption of molecular oxygen, as the onset of oxygen desorption from $\text{Au}(111)$ is observed at $\sim 400 \text{ K}$ [9].

STM images were collected at room temperature, and Z-channel as well as I-channel images were obtained simultaneously. The sample bias voltage was set to +1 V. Etched $\text{Pt}_{0.8} \text{Ir}_{0.2}$ tips from Molecular Imaging were used for imaging.

Results and Discussion

Oxygen ion sputtering of $\text{Au}(111)$ surfaces introduces a rough surface morphology as illustrated by the STM images shown in Fig. 1. For this particular preparation the Au surface was exposed to a fluence of $\sim 6 \times 10^{15} \text{ O}_2^+ \text{ ions/cm}^2$ (corresponding to $\sim 9 \text{ ML}$). After annealing to 400 K (10 minutes), AES reveals an oxygen coverage of $\sim 0.2 \text{ ML}$. The sputtered surface remains relatively smooth on a large scale (Fig. 1a), and the original step-terrace structure can still be observed. However, a close-up view of the image (Fig. 1b) reveals the development of a rough surface morphology consisting of mounds and pits. The symmetry of both, mounds and pits, reflects the hexagonal symmetry of a (111) surface, and the length scale of the pattern is

~ 15 nm (Fig. 1b). A similar surface morphology has been observed after Ar^+ ion bombardment of Au(111) surfaces [10,11]. The line scan shown in Fig. 1c reveals a short range surface roughness of up to ~1.0 nm (corresponding to 4 monoatomic steps).

The rough surface morphology of oxygen ion sputtered Au(111) (Fig. 1) is modified by tip-sample interactions during imaging. Figure 2 shows an area of the sample which has been modified during a previous scan in the upper part of the image: the length scale of the pattern increases as mounds and pits coalesce, and the corrugation decreases from ~1.0 nm (4 monoatomic steps) to ~0.25 nm (1 monoatomic step) as illustrated by the line scan shown in Fig. 2, bottom. Notably, this phenomenon was only observed immediately after the tip was cleaned by applying 10 V pulses (to another area of the sample) — a procedure that repetitively yields a tip that exhibits metallic behavior, as judged by the observed current (I) vs. voltage (V) curves.

The depletion of adsorbed oxygen and the deposition of S on oxygen-sputtered Au(111) surfaces during exposure to SO_2 was monitored by AES. The oxygen coverage decreases with increasing SO_2 exposure, as revealed by the decreasing $\text{O}_{519}/\text{Au}_{239}$ AES peak ratio (Fig. 3, open symbols). The deposition of sulfur is delayed, and only observed after the initially adsorbed oxygen completely disappeared based on the $\text{S}_{150}/\text{Au}_{239}$ AES peak ratio (Fig. 3, full symbols). The depletion of oxygen is not caused by electron-stimulated oxygen desorption during AES data collection, as consecutive Auger spectra collected in the absence of SO_2 do not result in a decreasing $\text{O}_{519}/\text{Au}_{239}$ AES peak ratio. Annealed (squares/ triangles) and as-sputtered (circles) surface preparations exhibit the same behavior with respect to oxygen depletion and sulfur deposition.

The decreasing oxygen coverage with increasing SO₂ exposure suggests that chemisorbed oxygen on Au(111) surfaces can be abstracted by impinging SO₂ molecules via SO₃ formation [12]:



The deposition of sulfur is only observed *after* oxygen is *completely* removed. The observation of S deposition is most likely due to disproportionation of SO₂ into adsorbed S and SO₃ followed by abstraction of the residual oxygen by another SO₂ molecule. As the oxygen released by SO₂ decomposition is not detected by AES, oxygen removal by SO₂ must be considerably faster than SO₂ decomposition. Indeed, the rate of oxygen abstraction is roughly 4 times faster than the rate of SO₂ decomposition as judged by the experimental observation of the rates of oxygen depletion relative to sulfur deposition (Fig. 3).

The Au(111) surface exhibits an enhanced, transient reactivity towards SO₂ decomposition within the first one hundred Langmuirs of SO₂ exposure after reaching the oxygen depletion point (Fig. 4). The extent of this reactivity enhancement is strongly influenced by the experimental procedure: The step-like increase in the S-coverage at the oxygen depletion point is more pronounced if the Au surface is continuously exposed to SO₂ while reaching the oxygen depletion point (Fig. 4, squares and triangles). Specifically, a four times higher jump in the sulfur coverage is observed for continuous SO₂ exposure compared to an experiment where the SO₂ exposure was frequently interrupted for collecting AES data (Fig. 4, circles). This reveals that the surface reactivity towards SO₂ disproportionation decreases on a timescale of a few minutes (typical time necessary to collect AES data) after reaching the oxygen depletion point.

An oxygen-sputtered Au(111) surface exhibits a very rough surface morphology, and thus a high concentration of under-coordinated Au atoms, even after annealing to 400 K (Fig. 1). This is not a very stable configuration as demonstrated by the observation of tip-induced surface modifications during STM imaging (Fig. 2). Very similar surface morphologies have been reported for nanoporous Au, where it has been argued that chemisorbed oxygen stabilizes small pores and thus under-coordinated Au atoms present on these highly curved surfaces [13,14]. If under-coordinated Au atoms are indeed stabilized by chemisorbed oxygen, the depletion of oxygen during interaction with SO₂ should destabilize the rough surface morphology of an oxygen-sputtered Au(111) surface.

In a recent theoretical study, Rodriguez et al. [2] emphasized the enhanced catalytic reactivity of under-coordinated Au atoms. Specifically, the study demonstrates that under-coordinated Au atoms interact strongly with adsorbed SO₂, and decomposition is only slightly less favorable than desorption. The calculated activation barriers for decomposition and desorption of SO₂ on Au clusters consisting of 14 atoms are ~22 kcal/mol and ~15 kcal/mol, respectively. Similarly, an enhanced reactivity of small Au clusters on Au(111) towards O₂ adsorption was predicted by DFT calculations performed by Metiu et al. [15]. However, this study suggests that the enhanced reactivity is mediated by the shape of the HOMO/LUMO orbitals which in turn critically depends on the presence of undercoordinated Au atoms.

Following these results, we attribute the enhanced, transient reactivity towards SO₂ decomposition at the oxygen depletion point to the presence of undercoordinated Au atoms: oxygen adsorption stabilizes these sites but also blocks the catalytic activity.

Efficient SO_2 decomposition is observed only after all initially adsorbed oxygen is removed by reaction (I). Surface rearrangements on a timescale of a few minutes (triggered by oxygen depletion) explain the transient character of these highly reactive sites. Consistent with our experimental observations, this effect is more pronounced for unannealed Au(111)/O surfaces (annealing generally reduces the surface roughness).

The oxygen depletion observed in the present study suggests SO_3 formation. Formation of SO_3 was also observed during interaction of SO_2 with oxygen-covered Cu(110) and Ag(110) surfaces at 300 K [5,6]. However, on these surfaces, SO_3 does not desorb, but decomposes during consequent heating. The reaction energetics of the interaction of SO_2 with Cu, Ag, and Au (111) surfaces was previously calculated by Sellers et al. [7]. This study reveals that SO_2 can react with chemisorbed oxygen on Au and Ag surfaces towards SO_3 . In addition, distinct periodic trends for the reaction barriers of decomposition and desorption of SO_3 were reported: the barrier for SO_3 desorption decreases in the order Cu, Ag, Au (23 kcal/mol, 21 kcal/mol, 19 kcal/mol), whereas the barrier for SO_3 decomposition increases in the order Cu, Ag, Au (3 kcal/mol, 10 kcal/mol, 12 kcal/mol). These values suggest that desorption of SO_3 is more likely on Au than on Cu or Ag, consistent with our interpretation of the experimental results discussed above.

Our results contribute to a better understanding of the reactivity of highly dispersed gold nanoparticles. The enhanced reactivity of Au nanoparticles is generally interpreted as either a confinement effect or in terms of metal-support interactions. The present work, however, provides evidence that under-coordinated Au atoms can play an important role by increasing the reactivity, even in the absence of a specific metal-

support interaction. Our results are also consistent with more recent studies of oxygen adsorption on Au(111) performed in our group that indicate that structural changes in the surface that release Au atoms occur when oxygen is adsorbed and that these changes lead to enhanced reactivity of the surface [16,17].

Conclusion

Two reaction regimes were observed during interaction of SO₂ with O-sputtered Au(111) surfaces: oxygen removal and S deposition. The surface exhibits an enhanced reactivity towards SO₂ decomposition at the oxygen depletion point. This is attributed to the presence of highly reactive, under-coordinated Au species which are activated by oxygen depletion. The transient nature of these species explains the observed decrease in reactivity towards sulfur deposition within minutes.

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Figure Captions:

Figure 1: STM images showing the morphology of Au(111) following sputtering with oxygen ions at room temperature (fluence: $\sim 6 \times 10^{15} \text{ O}_2^+$ ions/cm²). (a) A large-scale image (500 nm x 250 nm) shows that the surface is relatively smooth on a large scale and that the original step-terrace structure persists. (b) A higher magnification image (125 nm x 62 nm) shows a rough morphology on a smaller scale consisting of mounds and pits. The pattern reflects the hexagonal symmetry of a (111) surface. (c) The surface roughness of ~ 1 nm (corresponding to 4 monoatomic steps) is demonstrated in the linescan along the line between A and B. The oxygen coverage is estimated to be 0.2 ML, based on the $\text{O}_{519}/\text{Au}_{239}$ AES peak ratio.

Figure 2: STM images of an oxygen ion sputtered Au(111) surface after tip-induced surface modification. The image is a zoom-out of a surface area that was previously scanned. The area that was previously scanned (top part) exhibits a different morphology: the islands coalesce and the corrugation decreases to 1 monoatomic step, as illustrated by the line scan along the line between A and B. 500 nm x 500 nm (inset: 125 nm x 125 nm).

Figure 3: Auger electron spectroscopy data showing the $\text{O}_{519}/\text{Au}_{239}$ AES peak ratio (open symbols) and the $\text{S}_{150}/\text{Au}_{239}$ AES peak ratio (full symbols) obtained from a Au(111) surface after sputtering with oxygen ions at room temperature (circles) as well as after annealing to 400 K (squares/triangles) as a function of subsequent SO_2 exposure

at 300 K. The oxygen coverage decreases with SO₂ exposure and the sulfur deposition starts after oxygen is completely removed.

Figure 4: Auger electron spectroscopy data showing the O₅₁₉/Au₂₃₉ peak ratio (open symbols) and the S₁₅₀/Au₂₃₉ peak ratio (full symbols) obtained from an O-sputtered Au(111) surface versus SO₂ exposure at 300 K. Three different preparations are shown: the circles represent the same data as those displayed in figure 3, where SO₂ exposure was frequently interrupted to collect AES spectra, the squares and triangles show oxygen and sulfur coverage for larger SO₂ dosing increments. The surface exhibits an enhanced transient reactivity towards SO₂ decomposition if SO₂ is continuously dosed at the oxygen depletion point (squares and triangles). This indicates the existence of transient highly reactive Au species.

Fig. 1

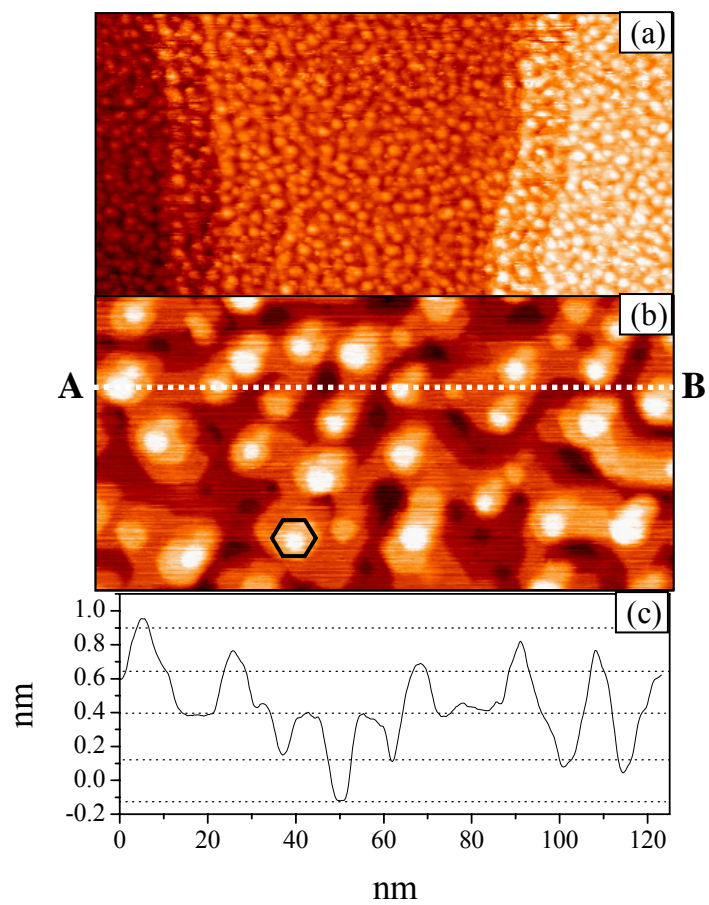


Fig. 2

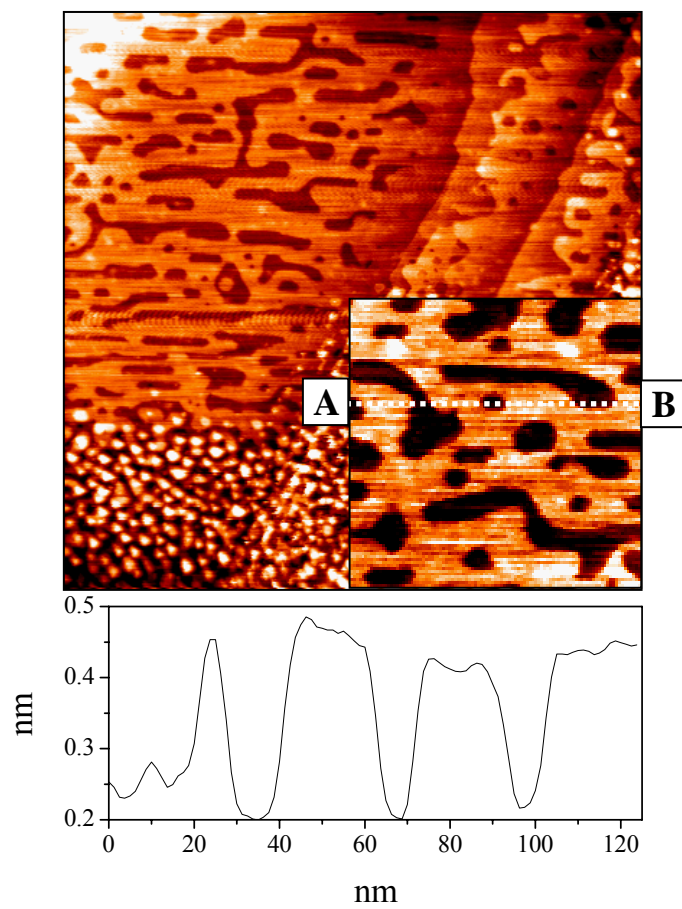


Fig. 3

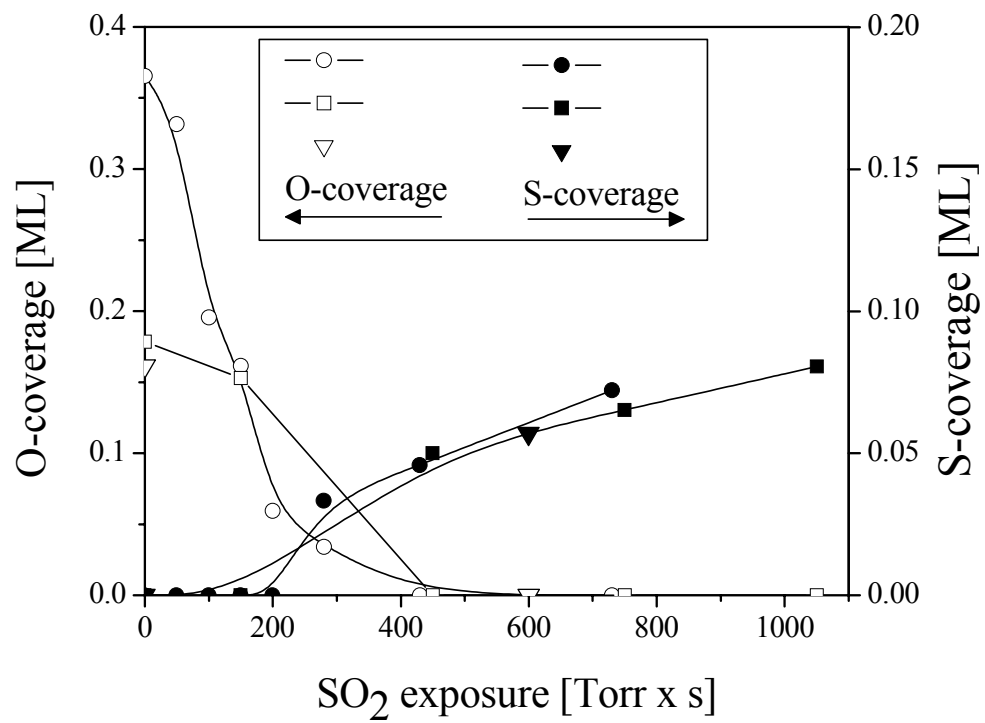


Fig. 4

